DIELECTRIC PROPERTIES OF A WATER MOLECULE PINNED ON THE SURFACE OF A SOLID BODY

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A model of the polarization of a water molecule pinned on the surface of a solid body by oxygen and hydrogen ions is studied. As the dielectric constant increases, the spark-over voltage of solid dielectrics decreases. The character of the contaminated surface (alkaline or acid) at the operating locations must be taken into account when designing insulators.

Water is a participant in biological and many technological processes. It is an important component and plays a decisive role in the technology of ceramic, composite, and other materials.

In the present article we perform mathematical modeling of polarization processes with the participation of molecular water in a wide range of frequencies on the basis of the theory of forced harmonic oscillations. Molecular water is always present in ceramic materials because of their porosity. For insulators which operate under atmospheric conditions, the contribution of molecular water to the permittivity can be appreciable. Water also plays an important role in the technology and operation of building materials.

Two variants of the pinning of molecular water on the surface of a solid body are possible: a molecule is pinned by an oxygen or hydrogen ion.

Let us consider the case where an oxygen ion pins a water molecule to the surface of a solid body. We shall assume that in the absence of an external field the molecule is in an equilibrium state. The constant dipole moment μ_0 of the molecule makes an angle θ_i with a distinguished direction which we shall assume below to be the direction of an external field. Under the action of an external, uniform, electric field E the dipole turns by an angle θ relative to the initial direction. In this case the external field engenders a torque [1]:

$$\mu = \mu_0 E \sin (\theta_i - \theta).$$

The molecule will be in equilibrium when the torque due to the external field equals the torque due to the quasielastic force striving to restore the dipole to its initial position:

$$\mu_0 F \sin \theta = \mu_0 E \sin (\theta_i - \theta),$$

where F is a quasielastic force which is also determined by, specifically, the coulomb interaction.

The projection of the dipole moment on the direction of action of the field is $\mu_0 \cos \theta_i$ before the dipole rotates and $\mu_0 \cos (\theta_i - \theta)$ after equilibrium is reached (Fig. 1).

In the absence of an external field, the dipole moments of water molecules sorbed by the dielectric are disoriented. The total dipole moment of the dielectric is zero. In an external filed, the dipole moment in the direction of the field will be different from zero [1]:

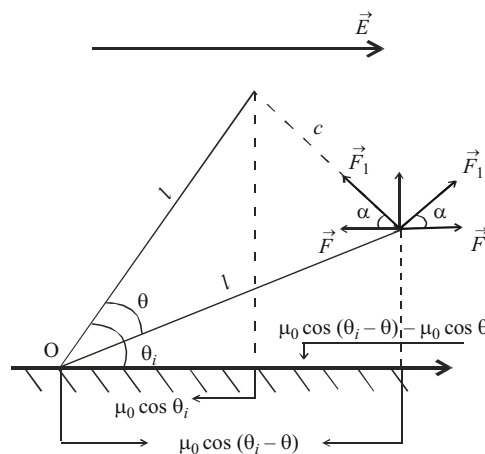$$\mu = \mu_0 \cos (\theta_i - \theta) - \mu_0 \cos \theta_i. \tag{1}$$

Fig. 1. Diagram showing the motion of the dipole of a water molecule pinned to the surface of a solid body by an oxygen ion.

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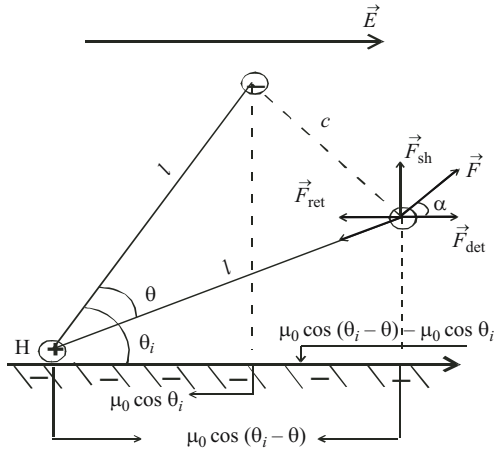
Fig. 2. Diagram of the motion of the dipole of a water molecule pinned to the surface of a solid body by a hydrogen atom.

If a harmonic external field is applied to the dielectric, then the molecule will execute forced oscillations. We assume that the oscillations of the molecule are linear and that the model of a linear oscillator can be used to describe the oscillations [2]. The angle θ is taken as the generalized coordinate to describe the angular oscillations and the moment of inertia of the molecule is used instead of the mass. We employed Shteiner's theorem [3] to calculate the moment of inertia of a water molecule pinned to the surface of a solid body by an oxygen ion. The result is:

$$I = 2.17 \times 10^{-47} \text{ kg} \cdot \text{m}^2.$$

The solution of the differential equation for θ is a complicated expression. Substituting the solution into the expression (1) we obtained the real and imaginary parts of the polarizability:

$$\alpha' = \frac{\mu_0^2}{2I} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + 4b^2\omega^2} ; \qquad (2)$$

$$\alpha'' = \frac{\mu_0^2}{I} \frac{b\omega}{(\omega_0^2 - \omega^2)^2 + 4b^2\omega^2} , \qquad (3)$$

where ω_0 is the frequency of the characteristic oscillations of a water molecule in the free state, ω is the frequency of oscillations of a water molecule in the pinned state; and, b is a damping coefficient.

We shall now examine the behavior of the polarizibility of a water molecule at different frequencies.

For $\omega = 0$ the polarizibility assumes the constant value

$$\alpha' = \frac{\mu_0^2}{2I\omega_0^2} ,$$

and there are no dielectric losses.

In an ac field with $\omega \ll \omega_0$ the real part of the polarizability of the dipole remains constant but the losses increase with frequency. Near resonance, where $\omega \sim \omega_0$, $b \ll \omega_0$, and $\omega_0 - \omega = \Delta\omega$, the polarizability and the losses assume their maximum values.

To determine the dielectric constant, which is a macroscopic characteristic that is taken into account in practical questions, its variation as a function of the frequency of the external electric field from ultraviolet to technical frequencies is studied.

Electronic elastic polarization is observed in the ultraviolet range ($\omega = 10^{17} - 10^{15}$ Hz). In this case the dielectric constant will be equal to its value for a water molecule in a free state: $\varepsilon'_e = 2.055$ [4].

Intramolecular ionic elastic polarization is observed in the infrared range ($10^{14} - 10^{12}$ Hz), but the reduced mass of the ions participating in the oscillation process (stretching and flexural vibrations) is taken instead of the electron mass. The polarizability in the region $\omega \ll \omega_0$ is calculated as

$$\alpha' = \frac{2q^2}{M_n \omega_0^2} ,$$

where q is the electron charge and M is the molar mass of the electrons.

The dielectric constant in the region $\omega \ll \omega_0$ is equal to that of a free water molecule studied in [4]: $\varepsilon'_u = 4.84$.

Librational oscillations of the water molecule contribute to the elastic dipole polarization.

The characteristic vibrational frequencies of a water molecule in the IR spectrum are [5]: $\omega_{01} = 4.02 \times 10^{14}$ sec^{-1}, $\omega_{02} = 1.32 \times 10^{14}$ sec^{-1}, $\omega_{03} = 0.32 \times 10^{14}$ sec^{-1}. The values of the polarizability for elastic dipole polarization are: $\alpha'_1 = 0.00546 \times 10^{-41}$ fm^2, $\alpha'_2 = 5.066 \times 10^{-41}$ fm^2, $\alpha'_3 = 87.07 \times 10^{-41}$ fm^2. The dielectric constant is $\varepsilon'_d = \frac{n(\alpha'_1 + \alpha'_2 + \alpha'_3)}{\varepsilon_0} = 3.48$.

The high-frequency permittivity taking account of the electronic, ionic, and dipolar elastic polarizations is $\varepsilon' = \varepsilon'_e + \varepsilon'_u + \varepsilon'_d = 8.32$ (for a free water molecule $\varepsilon' = 8.57$ [4]).

The rf permittivity (for characteristic vibrational frequency of a water molecule $\omega_0 = 5.45 \times 10^{12}$) is $\varepsilon' = 83.32$.

We shall now examine the case where a hydrogen ion pins a water molecule to the surface of a solid body (Fig. 2). The component of the dipole moment in the direction of the field is calculated using Eq. (1). The angle θ is determined from the problem of the vibrations of a water molecule, which a hydrogen ion pins to the surface of a solid body, in an ac electric field. The molecule executes forced oscillations described by a differential equation.

The moment of inertia of a water molecule pinned to the surface by a hydrogen ion can be calculated similarly to the moment of inertia of a molecule pinned by an oxygen ion but

the mass of a hydrogen atom is substituted into the formula. The moment of inertia is $I = 17.21 \times 10^{-47}$ kg $\cdot$ m^2.

Just as in the case of a water molecule pinned by oxygen, the polarizability has a similar form but since the moment of inertia is different the polarizability also differs substantially in magnitude.

For $\omega = 0$ $\alpha' = 1.12 \times 10^{-37}$ and the imaginary part of the polarizability is zero. Correspondingly, the permittivity changes substantially:

$$\varepsilon = 1 + \frac{n\alpha'}{\varepsilon_0} = 280,$$

where n is the concentration of a mole of water per unit volume and $n = 3.34 \times 10^{28}$ m^{-3}.

Thus, the permittivity of water will differ substantially, depending on the pH of the surface of the solid body. This will affect the rheological and electrolytic properties of substances.

In the case of pinning by oxygen the permittivity ($\varepsilon_0 = 8.32$) is somewhat less than the permittivity of free water at these frequencies ($\varepsilon' = 8.57$). At rf frequencies $\varepsilon' = 83.22$.

For pinning by hydrogen the IR-range permittivity of a water molecule pinned by a hydrogen ion is less ($\varepsilon = 5.265$) than at rf frequencies ($\varepsilon' = 14.715$).

The calculations performed in this work show that the permittivity of a water monolayer, characteristic for the surface of insulators with relative humidity of the surrounding air up to 60%, differs by a factor of 100 depending on the surface pH. This must be taken into account when developing the composition and technology for obtaining glazes for insulators. When designing insulators, the character of the surface contamination (alkaline or acidic) at the operating locations must be taken into account.

Ordinarily, glass surfaces and, presumably, porcelain surfaces are covered with a layer of moisture which is no more than a monolayer with relative humidity not exceeding 60%. As the humidity increases, the film thickness can reach 100 or more moleculer layers (see Fig. 1) [6].

The experimental data show that the permittivity of a solid dielectric affects the spark-over voltage. As the permittivity increases, the spark-over voltage of solid dielectrics decreases.

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